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OPTIMIZATION OF FERRITIC STEEL POROUS SUPPORTS FOR PROTONIC FUEL CELLS WORKING AT 600°C

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ABSTRACT: Porous alloys are used as supporting structures in high temperature fuel cells. A novel concept is to fabricate metal supported protonic conducting fuel cells working at 600°C. This fuel cell type offers several advantages for using porous alloy substrate in comparison to an oxygen conducting solid oxide fuel cell. In this work corrosion properties of a Fe22Cr0.4Mn alloy in porous form are evaluated in humidified hydrogen at 600°C and a method to improve its corrosion resistance is reported. Supports in the not modified state corrode rapidly by formation of dual phase oxides whereas after the modification by preoxidation supports offer high corrosion resistance allowing construction of fuel cells.

Keywords: porous stainless steel, corrosion, protonic fuel cell, protective coating, infiltration, preoxidation.

1. INTRODUCTION

Fuel cells are energy conversion devices that use fuel and oxidant to electrochemically convert them into electrical energy and heat. Several fuel cell types exist with most common being low temperature (< 200°C) polymeric electrolyte fuel cells (PEMFC) and medium/high temperature Solid Oxide Fuel Cells (SOFC) [1]. High temperature fuel cells offer high conversion efficiencies and are flexible with possible fuels.

Metal supported solid oxide cells have been gaining popularity in the recent years [2,3]. In comparison to traditional, all ceramic (or ceramic and cermet based) they offer the advantage of lower cost and improved heat transfer inside the cell. Metallic alloys have been first introduced as a replacement for ceramic interconnects in high temperature electrode supported fuel cells and more recently due to progress in the fabrication methods and novel materials metallic alloys have been proposed as supporting structures for ceramic layers. These changes in the design of fuel cells have been named 2nd and 3rd generation of cells respectively.

A schematic diagram of a typical planar fuel cell is presented in Figure 1. Also typical thicknesses of layers are given. It is evident that the support constitutes a majority of the materials volume.

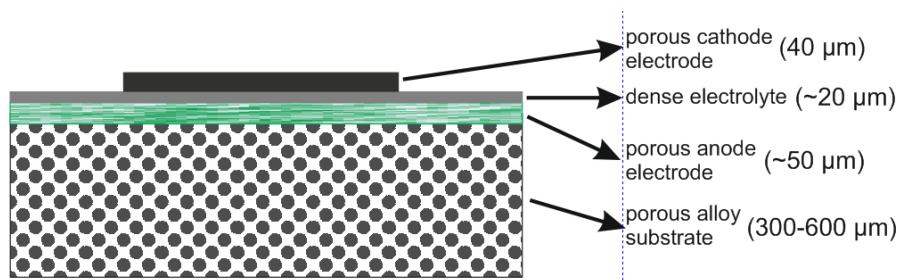


Figure 1. Schematic diagram of a planar fuel cell construction.

Metal supported solid oxide fuel cells, built on the base of oxygen conducting electrolyte have been reported by several research groups [2,3]. However metal supported protonic fuel cells are a new research topic. Using protonic conducting electrolyte has several advantages for the metal supported cell structure. Firstly, working temperature of protonic electrolytes lies usually around 600°C which can be regarded as a relatively low temperature for a metallic support. For oxygen conducting membranes working temperature is typically above 650°C and can go up to 800°C. Secondly, the steam in protonic fuel cells is produced on the cathode side, thus the porous metal support is subjected to a constant atmosphere of humidified hydrogen.

When exposed to oxidizing atmosphere, all metallic alloys form thermodynamically stable oxides on their surface. This process is thermally activated and thus at high temperatures ($> 500^{\circ}\text{C}$) its kinetics can be high. Formation of the oxides changes electrical and mechanical properties and in case of porous alloys will also lead to a decrease of the porosity.

Due to fuel cell working requirements, metal support needs to fulfil several criteria:

- Needs to be chemically and structurally stable in the anode atmosphere (humidified hydrogen).
- To ensure gas permeability support should have porosity higher than 20%.
- Formed oxide scale must be electronically conductive.
- Thermal expansion coefficient of the alloy should closely match that of other cell components.

Due to the above requirements mainly ferritic stainless steels have been proposed as porous supports for fuel cells. These are iron based alloys with high chromium content (between 16 and 26 wt.%). During oxidation they form a protective chromia scale which at high temperatures is sufficiently conductive. Thermal expansion coefficient of the ferritic structure is usually below $12 \times 10^{-6} \text{ K}^{-1}$.

Porous alloys are formed by sintering alloy powders in highly reducing atmosphere. Powders can be shaped by several methods including pressing/compaction, extruding and tape casting. The latter one is most commonly used to fabricate supports for planar fuel cells as it is relatively simple and cost effective. In most of the reported metal supported designs, the support is co-sintered with the ceramic layers deposited on top of it. This approach has the advantage of high production throughput but it is hard to match all shrinkage and sintering profiles for a multilayer structure. Another approach is to deposit ceramic layers on already sintered metallic supports. In this way the ceramic layers have to be deposited in the dense state not requiring any further high temperature sintering. This methodology offers more flexibility to the selection of the materials.

High temperature corrosion properties of porous alloys for use in fuel cells have been only partially studied. There exist only a limited number of commercially available materials in the powder form that fulfil the requirements. Many factors directly influence the corrosion performance of the porous alloys: mainly porosity, surface area, particle size, sintering temperature and atmosphere and others. Due to a relatively low surface area of the sintered alloys ($< 0.02 \text{ m}^2 \text{ g}^{-1}$) it is hard to measure specific surface area on small samples or on samples prepared by compacting/pressing. In this way it is often not possible to give a relevant corrosion data in terms of corrosion rate expressed per unit surface area. Instead sometimes a percentage weight gain is reported. This is however always different for differently prepared samples.

In the available literature several publications have been devoted to studying properties of porous alloys at high temperatures. Mostly these works have focused on the temperature range above 700°C. Matus et al. [4] studied a porous Fe30Cr (30 wt.% of Cr) alloy as a support of a Solid Oxide Fuel Cell working at 900°C. Fabricated cells showed a potential for rapid thermal cycling (heating and cooling rates $\sim 50 \text{ K min}^{-1}$). No long term aging was performed on these alloys. Bautista et al. [5] studied corrosion behaviour of ferritic Fe22Cr, AISI430L and austenitic Ni20Cr and IN625 alloys at 800°C. Porosity of different samples ranged from 22 to 35 %. All studied alloys corroded heavily filling pores with oxides even after relatively short oxidation times of 200 hours. The expected lifetime of the high temperature fuel cells are in the range from 10000 hours for portable applications to 40000 hours for stationary systems. Relatively lower corrosion rates were reported for ferritic alloys which formed chromia scale whereas austenitic alloys formed not protective nickel oxide scales. Molin et al. [6–8] studied porous 316L, 430L and IN600 alloys at 800°C. All alloys degraded rapidly in air over the 1000 hours test. Authors reported a rapid and severe decrease in open porosity that would block gas access to the electrodes. Several more reports from high temperature exist [2,9]. Only a limited number of works focused on the development of metal supported cells at 600°C or below [10,11]. Hui et al. [10] used a porous 430 alloy to fabricate fuel cells operated up to 600°C. Though the polarization resistance was quite high at 600°C due to the use of not optimized materials, the degradation over the test time of 11 days was low. It therefore shows the potential to use porous metal supports at reduced temperatures.

This work focuses on description of corrosion and structural properties of a ferritic alloy proposed as an anode side support for protonic fuel cells working at 600°C. Potential of extending alloy performance by a peroxidation procedure is presented.

2. EXPERIMENTAL PROCEDURE

Porous alloys were produced by Höganäs AB company located in Sweden. Alloy powders were produced by water atomization process. Produced powders were then sieved through $-53\ \mu\text{m}$ mesh and were used for preparing the tape casting slurry. After tape casting tapes were sintered in hydrogen at 1250°C for 30 minutes.

Corrosion properties of porous specimens were evaluated at 600°C by placing samples in an alumina sample holder in a tube furnace. Samples with dimensions of $2 \times 2\ \text{cm}^2$ were cut from sintered tapes and a small hole was punched for hanging on a platinum wire. Samples were separated with alumina spacers and placed parallel to the flow direction. Mixture of hydrogen/nitrogen (9/91 vol.%) was purged through a water bubbler held at room temperature (~ 4 vol.% of steam content) and introduced to the furnace. Samples temperature was monitored with a thermocouple placed close ($< 1\ \text{cm}$) to the samples. Oxidation temperature was 600°C and ramping rates for heating and cooling were $120^\circ\text{C}/\text{hour}$. Weight gain of samples was measured firstly on the as-received and cleaned samples and then after the desired oxidation time. Weight gain of samples in this work is expressed as a relative weight gain in respect to the initial sample weight.

The preoxidation of porous alloys took place in a tube furnace with flowing dry hydrogen/argon mixture (9/91 vol.%). Preoxidation temperature was 700°C , 800°C or 900°C with ramping rates of $120^\circ\text{C}/\text{hour}$ and holding time of 1 hour.

Samples microstructural analysis was performed using a Hitachi TM3000 scanning electron microscope (SEM) equipped with an energy dispersive x-ray spectrometer (EDS). Sample surfaces and cross sections were analysed. Cross sections were prepared by embedding samples in epoxy and then polishing down to $1\ \mu\text{m}$ finish using diamond slurry. For microscopy samples cross sections were coated with carbon.

3. RESULTS AND DISCUSSION

Alloy composition (analysed from the sintered tape) selected as a candidate material for protonic fuel cell support is given in Table 1. Addition of Mn to alloy composition should allow for formation of a Mn,Cr spinel on top of the chromia scale. This oxide has been shown to be beneficial for interconnects of high temperature fuel cells. Level of impurities and undesired elements (Si, Al) is very low.

Table 1. Chemical composition of the as-sintered tape (wt.%).

	Fe	Cr	Mn	Ni	Mo	Cu	Si	Al	Nb	W	C	O	N	S
Fe22Cr0.4Mn	bal.	22	0.23	0.03	0.01	0.02	0.08	0.00	0.02	0.00	0.01	0.03	0.01	0.00

Images of the surface and of the polished cross section of the as-sintered alloy are shown in Figure 2. Porosity of the support as determined by image analysis (ImageJ, NIST, USA) is $\sim 24\%$. Particle size of the alloys, used for the preparation of tapes, achieved through a sieving process were larger than $53\ \mu\text{m}$. Image shows well sintered particles with the porosity being made of large pores. This should enable easy gas flow to the electrode deposited on top of the support.

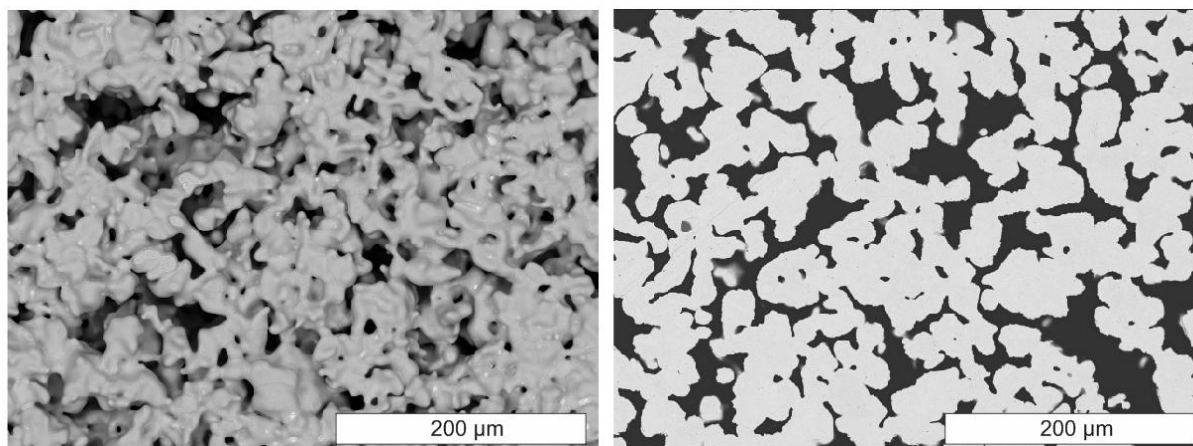


Figure 2. SEM images of surface and polished cross section of as-sintered support.

3.1 Corrosion properties of the as-sintered alloy

As-prepared tapes were evaluated for their corrosion resistance in humidified hydrogen at 600°C. This atmosphere is resembling the anode conditions of the protonic fuel cell. The calculated equilibrium pO_2 of such atmosphere is 2.5×10^{-25} atm (calculated assuming 4 vol.% of steam). Although this is a very low value, it is thermodynamically in the oxide formation region.

Weight gain of the Fe22Cr0.4Mn alloy measured at 600°C is shown in Figure 3.

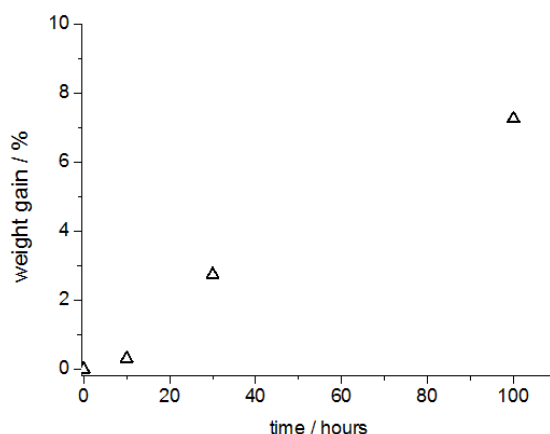


Figure 3. Weight gain of the porous Fe22Cr0.4Mn support at 600°C in humidified hydrogen.

Weight gain is caused by the oxidation of chromium, iron and manganese. In an ideal case chromium oxidizes and forms a passivating layer of chromium oxide that further protects the substrate. In case of iron oxidation, the iron oxide is not regarded as protective and would not stop further oxidation of the support leading to a catastrophic degradation. Measured weight gain is showing only the oxygen pick up, the consumption (or depletion) of metal from the support can be assessed by assuming chemical reactions:



As oxygen is much lighter than chromium and iron, during the formation of the oxide a considerable amount of Fe and/or Cr is drawn from the substrate thus changing its properties.

Over a relatively short time of 100 hours weight gain reaches 8 wt.%. This is a very high gain even when compared to results obtained at 800°C by other authors on similar alloys.

SEM image of cross sections of oxidized Fe22Cr0.4Mn alloy is shown in Figure 4. Support corroded quite heavily showing many corrosion products. However they seem to form not uniformly over the alloy volume. Clearly the top side of the Figure 4 A is corroded much more than the bottom side of the sample. These samples were prepared by a tape casting process, where usually one side has lower surface roughness as it was deposited directly on the carrier film. This might be one reason for different properties. Other possibility is that during the sintering on alumina substrate some alumina diffuse into the substrate and change its oxidation properties as well. Traces of alumina have been indeed detected on the surface of the sintered tape.

In Figure 4 B a higher magnification of the corrosion products is shown. This oxide is a dual layered compound with an inner layer of chromium oxide and an outer layer of an iron oxide as described below. At some places, almost no corrosion scale is detected (most of the bottom side of Figure 4 A and in Figure 4 B below the oxide). It seems that the support oxidized only in some selected areas that must have had lowered oxidation resistance.

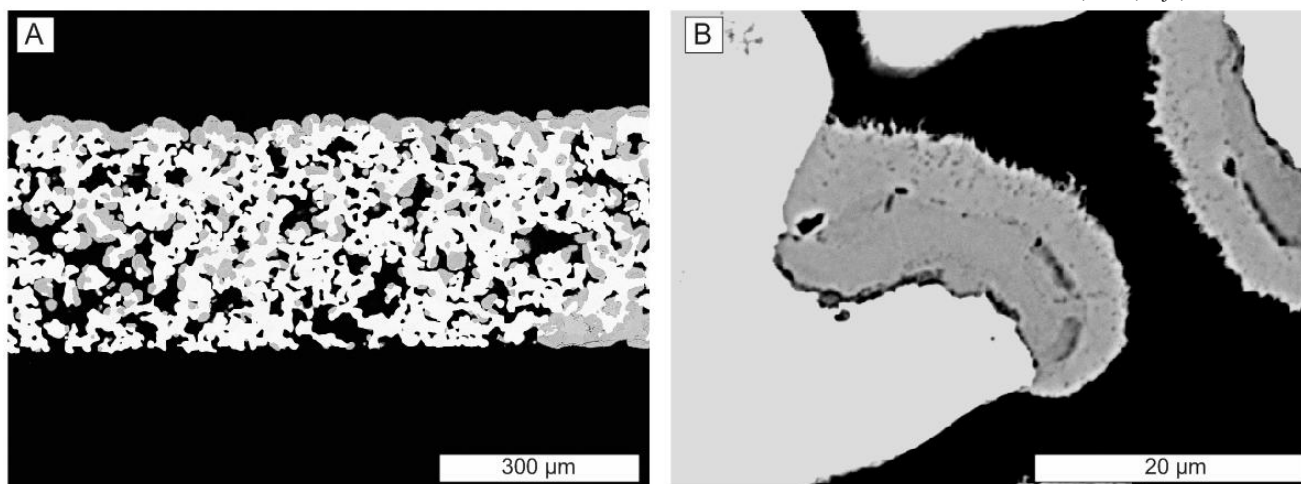


Figure 4. SEM images of oxidized Fe22Cr0.4Mn alloy.

By SEM/EDS analysis of the sample cross section it has been confirmed that the oxide formed is a mixture of chromium oxide and iron oxide. Figure 5 shows the EDS mappings of Cr, Fe, Mn and O. In the Figure several oxide formations are visible. All of them tend to be dual compounds. The first layer is always a chromium rich oxide with some iron addition (based on Cr_2O_3) and the outer layer is iron based oxide (in this case FeO). No other corrosion products are detected. As the weight gain for sample is high and the oxide thickness at some places is high, the composition of the alloy grain that is covered by the thick oxide was performed to determine its compositional change caused by oxidation. For comparison grain without the excessive corrosion was also tested. In comparison to the not heavily oxidized grain, the chromium content in the heavily oxidized grain was higher (~24 wt.% to ~22 wt.%). Although considerable amounts of Cr and Fe are drawn from the samples during the formation of the layered oxide, the resulting composition of the grain does not change much. It is still far away from the usually regarded breakaway oxidation threshold (~15 wt.% of Cr content [12–14]). More studies should be devoted to clarifying the reason for excessive corrosion occurring only at selected spots.

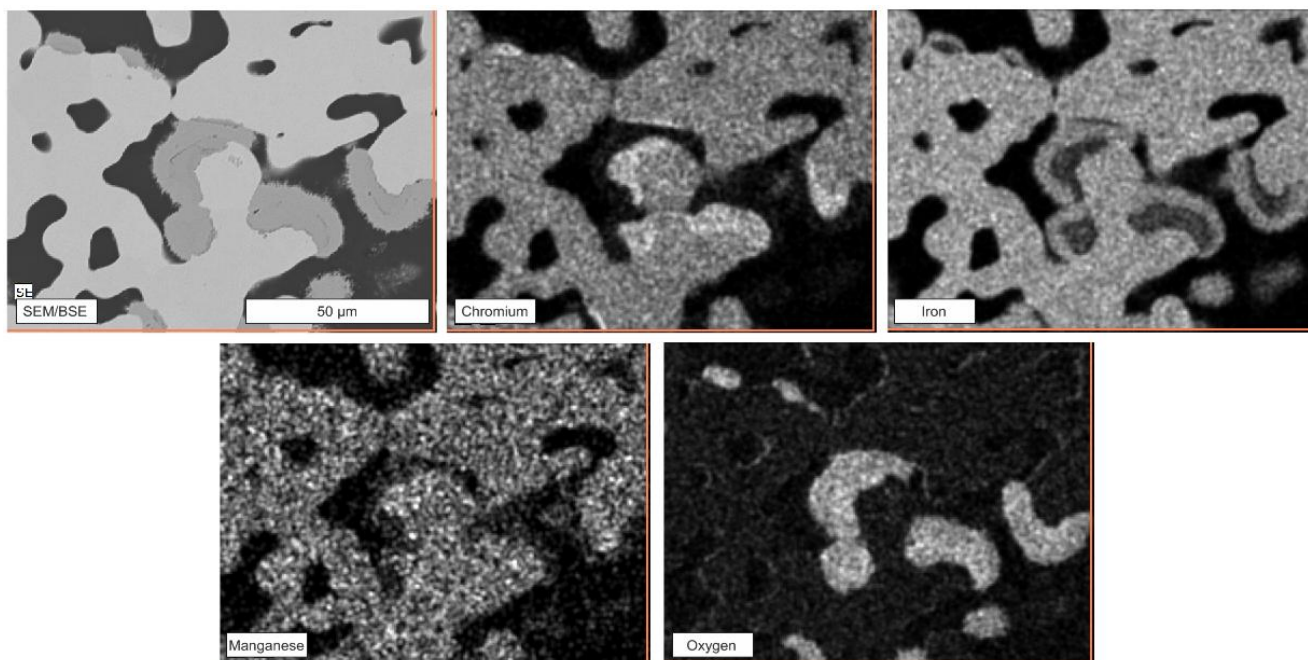


Figure 5. Weight gain of the porous Fe22Cr0.4Mn support at 600°C in humidified hydrogen.

Although the reasons for high corrosion rates of some regions of the alloys are not yet identified, in places that did not undergo excessive corrosion the oxide layer after 100 hours of studies at 600°C is hardly visible. The pristine corrosion resistance of the alloy with no defects is thus probably high enough. To ensure improved overall properties of the support surface modifications can be considered. This should serve to stabilize the surface and thus limit corrosion.

To mitigate excessive corrosion of the substrate, in this work an approach to improve oxidation resistance is presented. It is based on the preoxidation of the substrates at temperature higher than the operating temperature that can be easily implemented in the support or cell/stack fabrication.

3.2 Improvement of corrosion properties by preoxidation of porous alloys

By exposing samples to temperatures higher than 600°C formation of more protective chromia scale in the place of iron oxides is expected for iron based chromium rich alloys [15]. Due to a faster Cr diffusion and higher affinity to oxygen, at temperatures around 800°C chromia scale is preferably formed.

As the working temperature is predicted to be 600°C, preoxidation temperatures have been chosen to be 700°C, 800°C and 900°C. Samples were preoxidized in hydrogen atmosphere, as it offers more protective conditions for the substrates and lower initial corrosion.

Weight gain of samples after the preoxidation in hydrogen are presented in Figure 6. With the increase of the temperature the weight gain is higher as expected. Weight gain measured after oxidation at 700°C and 800°C are close to 1 wt.% whereas weight gain after 900°C is 2 times higher. Weight gain at 700°C is however unexpectedly high.

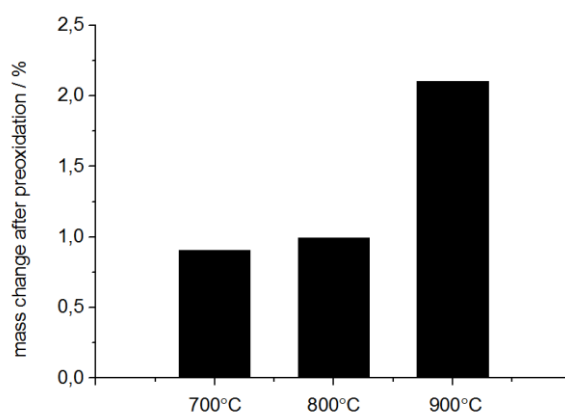


Figure 6. Weight gain of the porous Fe22Cr0.4Mn support after preoxidation at different temperatures in hydrogen.

SEM images of preoxidized samples are shown in Figure 7 A-C. On samples preoxidized at 700°C and 900°C some new oxides grown on the surface with diameter of 2-3 µm are easily distinguishable. By EDS analysis these are characterized as iron rich oxides. For sample oxidized at 700°C it might explain the weight gain being close to the sample oxidized at 800°C.

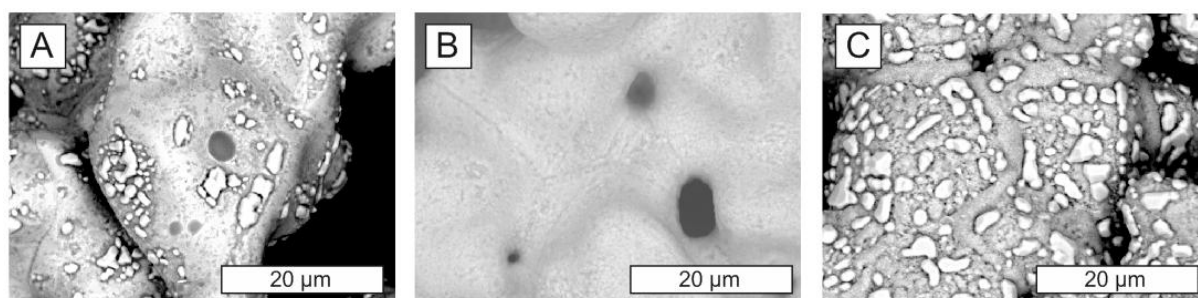


Figure 7. SEM images of the porous support after preoxidation at different temperatures in hydrogen. A - 700°C, B - 800°C, C - 900°C.

Based on the presented results the preoxidation temperature for samples for corrosion testing has been chosen to be 800°C where a thin uniform chromia based oxide is formed.

Weight gain of a reference, not preoxidized sample in comparison to a preoxidized sample are presented in Figure 8. For easier data comparison the weight gain axis is presented in logarithmic units. The weight gain of the preoxidized samples is

much smaller and its increase rate is steady and small. The data for preoxidized alloys does not include the initial weight gain caused by the preoxidation, but even including that it is still much smaller. The oxides on the surface of the preoxidized alloy even after 500 hours of oxidation at 600°C are hardly visible. Therefore the method is suitable for improving corrosion properties of porous alloys. It can be also easily included into a technological processes. Support might be exposed to higher than the operating temperature during sealing or reduction step of a fuel cell. Even a short time exposure (1 hours) results in a very stable operation.

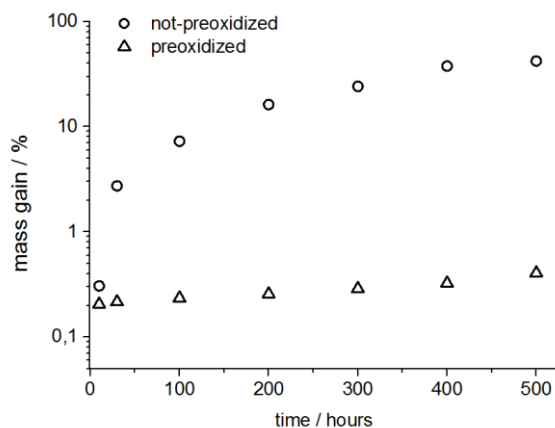


Figure 8. Weight gain at measured 600°C of not preoxidized and preoxidized porous alloy.

Conclusions

Dedicated iron based chromium rich porous alloys were fabricated to serve as supports for protonic fuel cells. Their corrosion properties were measured at 600°C in humidified hydrogen. As-received alloys oxidize rapidly, after 100 hours oxidation the weight gain almost reaches 10 wt.%. This high weight gain is due to excessive oxidation of selected areas of the support. Some areas remain not affected by corrosion at this relatively low temperature. In order to improve surface properties of porous alloy a surface modification by sample preoxidation was studied. Best results were achieved for preoxidation at 800°C for 1 hour in hydrogen/argon atmosphere. Preoxidized sample showed much smaller weight gain and much lower corrosion rate. This simple and effective modification method can thus serve as a solution to noted corrosion problems. Also the preoxidation can be implemented in support/fuel cell/stack fabrication stages relatively easily. Preoxidized porous alloys show properties that allow them to be used as successful supports on the anode side of protonic fuel cells.

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AUTHOR DETAILS

S. Molin defended his Ph.D. at Gdansk University of Technology in Poland on the topic of fabrication and characterization of metal supported cells in 2011. From 2012 he holds a PostDoc position at the Department of Energy Conversion and Storage at Technical University of Denmark in Roskilde, Denmark (Risø Campus). His work includes high temperature corrosion of porous and dense alloys for high temperature use in solid oxide fuel and electrolysis stacks. Additionally he develops protective coatings to mitigate corrosion and protect other components.

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